

REPORT DOCUMENTATION PAGE			<i>Form Approved</i> OMB No. 074-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE January 13, 1998	3. REPORT TYPE AND DATES COVERED	
4. TITLE AND SUBTITLE First Report on Non-Thermal Plasma Reactor Scaling Criteria and Optimization Models			5. FUNDING NUMBERS N/A	
6. AUTHOR(S) Louis A. Rosocha, Richard A. Korzekwa				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Los Alamos National Laboratory			8. PERFORMING ORGANIZATION REPORT NUMBER LA-UR-98-125	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) SERDP 901 North Stuart St. Suite 303 Arlington, VA 22203			10. SPONSORING / MONITORING AGENCY REPORT NUMBER N/A	
11. SUPPLEMENTARY NOTES The United States Government has a royalty-free license throughout the world in all copyrightable material contained herein. All other rights are reserved by the copyright owner.				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release: distribution is unlimited.			12b. DISTRIBUTION CODE A	
13. ABSTRACT (Maximum 200 Words) The purpose of SERDP project CP-1038 is to evaluate and develop non-thermal plasma (NTP) reactor technology for DoD air emissions control applications. The primary focus is on oxides of nitrogen (NOx) and a secondary focus on hazardous air pollutants (HAPs), especially volatile organic compounds (VOCs). To design and build NTP reactors that are optimized for particular DoD applications, one must understand the basic decomposition chemistry of the target compounds and how the decomposition of a particular chemical species depends on the air-emissions stream parameters and the reactor operating parameters. This report is intended to serve as an overview of the subject of reactor scaling an optimization and will discuss the basic decomposition chemistry of nitric oxide and two representative VOCs, trichloroethylene and carbon tetrachloride, and the connection between the basix plasma chemistry, the target species properties, and the reactor operating parameters. System architecture, that is how NTP reactors can be combined or ganged to achieve higher capacity, will also be briefly discussed.				
14. SUBJECT TERMS NOx; VOCs; NTP; JETCs; HAPs;trichloroethylene; carbon tetrachloride; SERDP; SERDP Collection			15. NUMBER OF PAGES 16	
			16. PRICE CODE N/A	
17. SECURITY CLASSIFICATION OF REPORT unclass.	18. SECURITY CLASSIFICATION OF THIS PAGE unclass.	19. SECURITY CLASSIFICATION OF ABSTRACT unclass.	20. LIMITATION OF ABSTRACT UL	

LA-UR- 98-125

Approved for public release;
distribution is unlimited.

Title: FIRST REPORT ON NON-THERMAL PLASMA
REACTOR SCALING CRITERIA AND
OPTIMIZATION MODELS

Author(s): Louis A. Rosocha, CST-18
Richard A. Korzekwa, CST-18

Submitted to: Strategic Environmental Research &
Development Program (SERDP) Office and
to be made available for public
release.

Los Alamos
NATIONAL LABORATORY

DTIC QUALITY INSPECTED 1

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. The Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

First Report on Non-Thermal Plasma Reactor Scaling Criteria and Optimization Models

Prepared under Strategic Environmental Research & Development Program (SERDP)
Compliance Project CP-1038: Development of Non-Thermal Plasma Reactor
Technology for Control of Atmospheric Emissions

Louis A. Rosocha
Principal Investigator

and

Richard A. Korzekwa

Los Alamos National Laboratory

January 13, 1998

Introduction

The purpose of SERDP project CP-1038 is to evaluate and develop non-thermal plasma (NTP) reactor technology for Department of Defense (DoD) air emissions control applications. The primary focus is on oxides of nitrogen (NO_x) and a secondary focus on hazardous air pollutants (HAPs), especially volatile organic compounds (VOCs). Example NO_x sources are jet engine test cells (JETCs) and diesel-engine powered electrical generators. Example VOCs are organic solvents used in painting, paint-stripping, and parts cleaning.

To design and build NTP reactors that are optimized for particular DoD applications, one must understand the basic decomposition chemistry of the target compound(s) and how the decomposition of a particular chemical species depends on the air-emissions stream parameters and the reactor operating parameters. This report is intended to serve as an overview of the subject of reactor scaling and optimization and will discuss the basic decomposition chemistry of nitric oxide (NO) and two representative VOCs, trichloroethylene and carbon tetrachloride, and the connection between the basic plasma chemistry, the target species properties, and the reactor operating parameters (in particular, the operating plasma energy density). System architecture, that is how NTP reactors can be combined or ganged to achieve higher capacity, will also be briefly discussed.

A companion report, which deals with further aspects on the development of reactor-scaling algorithms and discusses a test-case hybrid-reactor system, has been completed under a subcontract managed by our Army Research Laboratory (ARL) team member Dr. Andrzej Miziolek. That project report is entitled "Development of Scaling and Economic-Evaluation Algorithms for Non-Thermal Plasma Reactors for Control of NO_x Emissions," and was produced by M. Matsuoka, S.J. Kim, P.C. Looy, and Prof. J.S. Chang of McMaster University (October 27, 1997).

In other SERDP-related work, economic projections for a pulsed corona discharge de-NO_x system for full-scale operation of Jet Engine Test Cells (JETCs) have been presented by S.M. Haythornthwaite, M.D. Durham, D. Rugg, and J.D. Wander in a report from ADA Technologies entitled "Application of Pulse-Corona-Induced Plasma to Jet Engine Test Cells." (under a contract managed by Dr. Joseph Wander of the Armstrong Laboratory).

Representative Non-Thermal Plasma Reactors

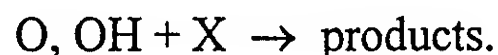
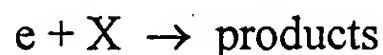
Figure 1 shows example NTP reactors for gas-phase pollutant processing [1, 2]. In an electrical discharge, a high voltage is applied across electrodes in the gas or along a surface adjacent to the gas. An electron-beam reactor requires an electron accelerator to produce the energetic electron beam (~ 100 keV - 1 MeV) that is injected into the process gas. The energetic plasma electrons are responsible for pollutant decomposition, either through direct electron collisions or indirectly through the creation of free radicals that attack the pollutants.

The three electric-discharge reactors - silent discharge (dielectric barrier), pulsed corona, and electrified packed bed all create transient electrical-discharge streamers in the gas. The streamer is the source of energetic electrons and other active species. A relatively high voltage (determined by the reactor geometry, gas composition, and gas pressure) is required to cause electrical breakdown in the gas. The necessary voltage is supplied by a drive circuit connected to the reactor. In corona, a non-homogeneous electric field is used to stabilize the discharge and prevent thermal arc formation. Silent discharges use charge buildup on a capacitive barrier to achieve a similar end result. An electrified packed bed is closely related to a barrier discharge. A surface-discharge reactor (not shown), which uses streamers across a dielectric surface, is similar to both the dielectric barrier and electrified packed bed reactors. Streamers can be thought of as cylindrical current filaments with typical radius ~ 100 μm . They are transient discharges (e.g., lasting only a few nanoseconds for oxygen or air), fed by ionization and detachment and then arrested when the electric field is reduced to the point where electron attachment becomes dominant. For streamers in pure oxygen and air, the average electron energy and electron density are $T_e \sim 3\text{-}5$ eV, $[e] \sim 10^{14}/\text{cm}^3$, while a typical breakdown reduced electric field strength in the gas is $E/N \sim 100 - 200$ Td. Multiple streamers typically give accumulated plasma energy loadings of 10s - 1,000s J/liter-atm [2].

In an electron-beam reactor, the source of electrons (the cathode) can be separate from the accelerating-field section (as in thermionic-cathode and plasma-cathode devices) or integrated with the accelerating-field section (as in a field-emission-cathode electron gun). Electron-beam reactors must use a foil or window to separate the vacuum section of the accelerator from the process gas. The electron beam penetrates the foil, depositing energy in the process gas by collisions and molecular excitation processes coupled to the creation of a large-volume non-thermal plasma. For typical electron-beam reactors, the mean electron energies can be much larger than those for discharge reactors (e.g., ~ 10 eV for electron-beam, as compared to \sim few eV for discharges). Similar energy loadings can usually be obtained in both types of reactors.

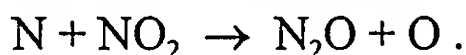
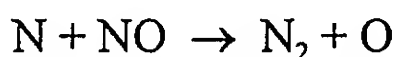
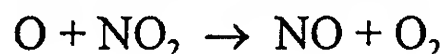
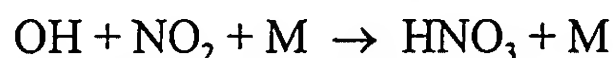
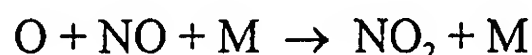
Basic Decomposition Chemistry

Plasma-generated active species (radicals and secondary electrons) are the initiators of pollutant decomposition reactions [1, 2]. Two major decomposition channels for a gas-phase chemical pollutant X are direct electron impact or chemical (radical-promoted) attack:



The first path is expected to dominate at large contaminant concentrations (when a higher energy fraction is absorbed by the pollutant), while the second should dominate at smaller concentrations.

The decomposition chemistry for NO is tractable and largely described as follows [1]:

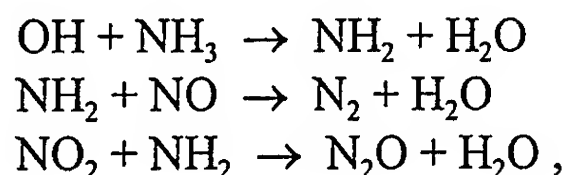


Oxidative-mode reactions involving O-atoms can trap total NO_x as NO and NO_2 . Oxidative-mode reactions involving OH-radicals produce nitric acid HNO_3 , which can be easily removed by a caustic scrubber. Reductive-mode reactions involving N-atoms instead drive more NO_x to N_2 and O_2 but require higher energy electrons.

With oxidative de- NO_x processes driven by O-atoms, NO_2 is the most probable reaction intermediate. It is somewhat more soluble in water than NO_x , which facilitates its removal by conventional wet-scrubbing techniques. However, for higher flow rates, the scrubber is usually impracticably large. The chemistry can be favorably influenced by multiple excitation, in which two or more NTP reactors are placed in series with scrubbers. Here the NO_2 reaction intermediate is scrubbed out at a low concentration before the gas is treated by the next reactor, thus reducing the conversion back to NO.

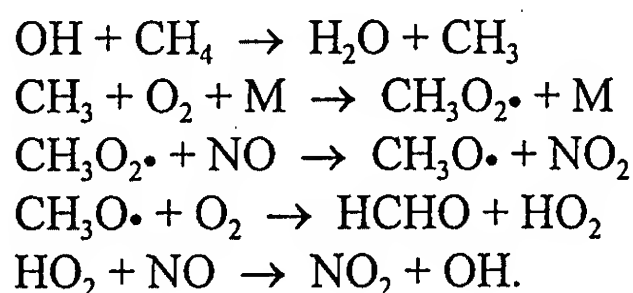
In wet gas (most representative of practical off-gas conditions), conversion to caustic-scrubbable nitric acid (HNO_3) is probably the most practical de- NO_x pathway. In a scrubber, nitric acid can also be converted to potentially useful byproducts, such as ammonium nitrate NH_4NO_3 agricultural fertilizer, by adding ammonia NH_3 . With humid gas, nitrous acid HNO_2 is also a significant reaction intermediate, which may decompose into NO and NO_2 . Multiple excitation, accompanied by intermediate filtration can probably also reduce such undesirable reformation of NO_x .

The addition of ammonia can also be used to advantage in further promoting reductive chemistry [1], as exemplified by the following reactions:



where the oxidative radical OH is replaced by the reductive radical NH₂.

There is some evidence in the literature to suggest that hydrocarbon additives can improve the efficiency of NO_x removal by regenerating OH-radicals. This is illustrated by the following reaction scheme using methane (CH₄) as a representative hydrocarbon.



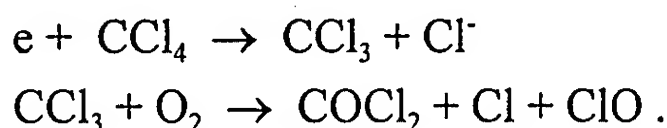
Experiments on pulsed corona performed at the Lawrence Livermore National Laboratory have provided corroboration of such effects by showing that the addition of n-octane (C₈H₁₈) improves the efficiency of NO removal [3].

Conventional de-NO_x technologies generally employ thermal-catalytic processes, scrubbing, and/or the addition of chemical additives (e.g., hydrocarbons, ammonia, urea compounds, isocyanic acid). The attractiveness of NTP-based technologies is the ability to initiate NO_x-removal chemistry similar to that of conventional process by employing electricity-based, selective chemistry (that might greatly reduce or even eliminate the need for large-scale chemical scrubbers).

Other molecules, like many VOCs, will often undergo a series of more complicated reactions before the final products result. The decomposition of a chlorocarbon like trichloroethylene is dominated by free-radical reactions at the relatively high E/N of electric discharges [4, 5]



Strong electron attachers (e.g., CCl₄) are preferentially decomposed by dissociative electron attachment at low E/N [6, 7]



Decomposition is not necessarily complete treatment - the goal is to produce less toxic or more easily managed final products. Byproducts must also be considered (e.g., COCl₂ is toxic but is easily removed by reactions with water). In laboratory studies, the degree of decomposition and treatment byproducts are measured with an instrument like a gas chromatograph - mass spectrometer or a set of combustion gas analyzers (CGAs), which may include a chemiluminescence detector for NO_x.

A key advantage of NTP processing is the ability to simultaneously remove multiple pollutants (e.g., several species of VOCs or VOCs in combination with NO_x and/or SO_x). The detailed plasma-initiated removal chemistry of a particular compound or mixture of compounds can be quite complicated and will not be further addressed in this report.

Decomposition-Scaling Relationships

In many non-thermal plasma devices (like gas lasers, ozonizers, etc.), a key process parameter is the specific energy (plasma energy density) deposited in the gas. This is also true for the decomposition of a pollutant in an NTP reactor. Experiments with various reactors have shown that the degree of removal of a particular contaminant depends on the applied plasma energy density \bar{E} , a characteristic energy-density parameter (which is related to the target compound), the carrier gas, and the reduced electric field E/N for the reactor [1, 2, 6].

Recent work on comparing different aqueous-phase advanced oxidation processes (AOPs) has shown that simple overall kinetic models can be used to describe the rate of radical-initiated decomposition of a target species [8]. Using an analogous description for a gas-phase AOP based on an NTP process, one can write the following expression for the decomposition of pollutant X in the presence of radical scavengers S_i

$$(1) \quad \frac{d[X]}{dt} = - \frac{G \bar{P} k [X]}{k [X] + \sum_i k_{S_i} [S_i]},$$

where $[X]$ is the pollutant concentration, G is the radical production efficiency, \bar{P} is the plasma power density, k is the radical-pollutant kinetic rate constant, $[S_i]$ is concentration of the i^{th} scavenger, and k_{S_i} is the scavenging rate constant for the i^{th} species.

Assuming an idealized reactor (constant E/N and carrier gas temperature), given the scavenger concentrations, and making the substitution $\bar{P} = d\bar{E}/dt$, one can integrate the above equation to get the pollutant concentration $[X]$ as a function of the starting concentration $[X]_0$ and the specific energy. When the rate of radical-pollutant attack $k[X]$ is small compared to the rate of radical scavenging $\sum_i k_{S_i} [S_i]$, the pollutant decomposition can be ideally expressed as

$$(2) \quad [X] = [X]_0 \exp (-\bar{E}/\beta),$$

where $[X]_0$ is the initial pollutant concentration, $[X]$ is the resulting concentration, \bar{E} is the applied specific energy (or plasma power divided by gas flow rate, P/Q), and β is the e-fold energy density

$$(3) \quad \beta = \frac{\sum_i k_{S_i} [S_i]}{k G}.$$

Supplying one β to the reactor reduces the concentration by $1/e$, 2β by $1/e^2$, and so on. In this ideal case, when $-\ln ([X]/[X]_0)$ is plotted versus \bar{E} , a straight line of slope $1/\beta$ results. For real cases, the plot is not necessarily a straight line, so such a slope-determined β -value is only an

approximation. In some cases, the removal function can additionally depend on the initial pollutant concentration. Figure 2 presents example decomposition data for two representative compounds, the flue gas nitric oxide (NO) and the chlorinated hydrocarbon trichloro-ethylene (TCE), C_2HCl_3 . The removal versus specific energy plots for neither of these two compounds shows a very strong dependence on initial concentration.

The β -value links the generation of radicals through gaseous electronics/plasma chemistry (G-values) with their utilization through the decomposition chemistry. The G-value is a function of an effective rate constant for radical generation k_{rad} (e.g., the dissociation rate constant for dissociating O_2 molecules into O-atoms), the electron drift velocity v_d , and the reduced electric field strength E/N

$$(4) \quad G = f \left(\frac{k_{rad}}{v_d \frac{E}{N}} \right).$$

The rate constant k_{rad} and the drift velocity v_d also depend on the reduced field E/N (electron temperature), so the β -value essentially depends on E/N and the chemical kinetics.

Reactor Scaling Concepts

The specific energy can also be expressed as

$$(5) \quad \bar{E} = P/Q = \bar{P} \tau_r,$$

where P and Q are the plasma power and gas flow rate, respectively, \bar{P} is the power density (power per unit volume) and τ_r is the residence time of a unit volume of gas in the active portion of the reactor.

To increase the removal fraction $[X]/[X]_0$ for a given gas mixture, the specific energy \bar{E} must be increased. \bar{E} can be increased by either increasing \bar{P} or τ_r (or, equivalently, decreasing the flow rate Q for a given cell volume). Assume the reactor volume is kept fixed. Therefore, to increase the removal fraction at a fixed flow rate, one can directly increase the power to the reactor. To increase the removal fraction at a fixed power, one can decrease the gas flow rate.

For a given reactor, the power and gas flow cannot be arbitrarily increased. Limits such as gas-flow impedance or heat conduction out of the reactor may limit the practical size of the reactor in terms of how much gas flow or deposited power can be achieved.

Additionally, the power density \bar{P} depends on the particular type of reactor being employed. Typically-achieved power densities for pulsed corona, dielectric-barrier, and electron-beam reactors are $< 15 \text{ mW/cm}^3$, 1 W/cm^3 , and 2.5 W/cm^3 , respectively [9]. Because of the lower spatial density of electrical discharges (smaller active volume compared to total gas volume) in pulsed corona reactors (PCRs), PCRs achieve a much smaller power density than dielectric-

barrier and electron-beam reactors. This implies a much smaller energy density at a given gas residence time.

Reactor Architectures

In the context of this report, architecture refers to the manner in which a NTP reactor, or combination of reactors and other equipment is configured to treat an emissions stream. At present, we assume that we will mainly deal with end-of-pipe emissions treatment (right before discharge to the air) for the DoD. The simplest end-of-pipe architecture is to employ an NTP reactor (or array) as a stand-alone emissions control device. Two basic reactor scaling architectures are discussed below: simply increasing the size of a single reactor (monolithic scaling) and parallel or ganged connection of smaller reactors (modular scaling).

Monolithic Scaling

To increase the capacity of an NTP reactor, we need to increase the gas flow rate. At a fixed removal fraction, the power must be increased in proportion to the flow rate. That is, if we scale up the flow by a factor N_s , the power must be scaled up by the same factor to keep the energy density fixed ($N_s P / N_s Q = P / Q$). This represents monolithic scaling, where we simply increase the physical size of the reactor while proportionally increasing the gas flow rate and plasma power.

Modular Scaling

Alternatively, the total gas flow and total plasma power can be divided among several reactor modules that are connected in parallel. The power to each reactor is then P / N_s , while the gas flow rate is Q / N_s (which keeps a constant energy density $P / N_s / Q / N_s = P / Q$). This represents modular scaling, whereby a reactor module of desirable properties is replicated many times, is quite attractive. Such modularization scaling of silent discharge cells has been previously demonstrated for the industrial-scale synthesis of ozone, where municipal water treatment plants frequently require the on-site generation of thousands of kilograms per day.

The modular approach has been employed at Los Alamos for scaling up both laboratory-scale and small, field-pilot-scale units. Typically, rectangular electrode-area, dielectric-barrier (silent discharge) reactors have been employed for VOC treatment tests [10, 11]. However, for systems requiring the treatment of higher temperature (e.g., > 100 C) emissions streams (sources of NO_x sources such as engines, etc.), cylindrical reactor cells may be more robust and practical in an engineering sense. Figure 3 illustrates a parallel array of dielectric-barrier plasma cells constructed of ceramic tubes with metalized electrodes, capable of elevated temperature operation. The summary results of electrical-performance characterization tests on a single module, which is a prototype for such an array, are presented in the Appendix.

However, because NTP reactors can be power intensive, neither monolithic nor modular reactors may be the most economic or practically-feasible architecture for very high flow applications. In that case, it might be better to consider yet another type of architecture, namely hybrid systems: an NTP reactor subsystem (or set of reactors) is combined with an absorber or catalytic subsystem. These concepts will not be further discussed here, but are the subject of another report entitled "Feasibility Analysis Report for Hybrid Non-Thermal Plasma Reactors".

Figure of Merit and Optimization

Optimizing the performance (degree of removal of the pollutant, decomposition products, energy consumption, etc.) of an NTP reactor is a complicated process. NTP processing is usually quite energy intensive. Therefore, in this section, we will concentrate on a discussion of reactor electrical energy consumption, because preliminary economic analysis indicates that the major cost of an NTP reactor system resides in the cost of the electrical power supply, assuming one uses readily-available power supplies - which are usually not well-matched to a plasma load. In some cases the power supply might be 75-90% of the plasma reactor cost. This cost is expected to fall with the development of better-matched, state-of-the-art power supplies and operation of the plasma reactor at more optimal treatment conditions.

A useful figure of merit for the decomposition of pollutants is defined by the energy delivered to the plasma per hazardous molecule removed from the gas stream. At any instant, this can be expressed as the following quantity obtained by solving Equation 2 for \bar{E} and taking the derivative:

$$(6) \quad \gamma_i = -\frac{d\bar{E}}{d[X]} = -\frac{d[-\beta \ln(\frac{[X]}{[X]_0})]}{d[X]} = \frac{\beta}{[X]}.$$

This is the instantaneous energy cost per molecule removed; a more practically-useful parameter is the integral, or average, energy cost γ

$$(7) \quad \gamma = \frac{\bar{E}}{[X]_0 - [X]} = \frac{-\beta \ln(\frac{[X]}{[X]_0})}{[X]_0(1 - \frac{[X]}{[X]_0})}.$$

Here, the energy cost per molecule is expressed in terms of the β -value, the degree of removal, and the initial concentration. As an example, Figure 4 gives \bar{E} , γ , and the reciprocal of γ , G (number of molecules removed per 100 eV of deposited energy) for a model TCE mixture. The γ -value translates into an actual electrical energy cost for the process. Another convenient unit for the figure of merit is the number of kilowatt-hours required to remove a kilogram of hazardous compound (i.e., kW-hr/kg). For a γ -value of 50 eV/molecule, approximately 10 kW-hr/kg of TCE are required. At an electrical energy cost of 5¢/kW-hr, TCE removal costs about 50¢ per kg (based only on the cost of energy into the plasma and neglecting other efficiency factors like that for the power supply and the cost of ancillary equipment).

Recently-presented work [12] on the fundamental limits for the removal of NO from engine exhaust gases, based on gaseous electronics and plasma chemistry considerations, has shown that the energy costs are 40 eV/NO molecule when reductive chemistry dominates and 18 eV/NO molecule when oxidative chemistry is dominant. Using the γ -value of 18 eV/molecule, approximately 15.7 kW-hr/kg NO removed are required. At the 5 ¢/kW-hr electrical cost figure, the NO-removal electrical cost is about 79 ¢/kg. It should be noted that the oxidative channel

principally results in the conversion of NO to NO₂, which does not change the total NO_x concentration a great deal. The reductive channel, which leads to N₂ + O₂ is preferable because less ancillary equipment (like an NO₂ trap/scrubber) is required in the de-NO_x system.

What Equation 6 tells us is that the instantaneous energy cost per pollutant molecule removed is lower when the pollutant concentration is high. This makes intuitive sense because, at high concentration, active species always have a high probability of reacting with a target molecule.

Equation 7 tells us that the average energy cost per removed molecule is lower at lower degrees of pollutant removal. In optimizing reactor performance, one can conceive of somehow adjusting the active species concentrations so that the ratio of pollutant concentration to active-species concentration is always relatively large. This way the probability of attack is high, while both the specific energy \bar{E} and the degree of removal ($[X]/[X]_0 \sim 1$) are low.

Two possible ways of achieving this optimization are constructing a continuous-flow reactor whose energy density decreases as the residence time of the treated gas in the reactor increases or constructing a serial train of reactors, each having optimal plasma energy density. One might even construct the first reactor such that it contains individual, segmented excitation regions (like a serial train within a single reactor).

Summary and Conclusions

The largest share of the present body of technical literature describing the treatment of air emissions with non-thermal plasmas (NTPs) mainly presents phenomenological descriptions of NTP reactor performance and, consequently in most cases, does not provide a consistent way to compare and/or predict the scaling and optimization properties of different NTP reactors. In this report, we have attempted to present a simple basis for comparing different types of NTP reactors, based on the concept of the plasma specific energy (electrical energy per unit volume deposited in the reactor active volume) required to remove a particular pollutant to a prescribed level in a defined exhaust-gas mixture.

It should be emphasized that NTP is an emerging air-emissions control technology. Very few (if any) commercial systems exist. Also, for many emissions applications, the present forms of NTP technology are expected to be expensive (in terms of electrical power consumption) and ancillary equipment (e.g., scrubbers) that may be necessary to handle treatment byproducts. Realizing the performance and economic shortcomings of stand-alone NTP reactors, some workers in this discipline have proposed the use of staged or hybrid systems to better match particular air-emissions control applications. In this case, overall system scaling must be considered in terms of the separate parts of the emissions-control system - that is the NTP reactor itself and the other major components. In this report, we have focused on the scaling and optimization concepts for the NTP part for two reasons: so that we can at least provide a simple means of making a first-order comparison of different NTP reactors and because the NTP part of the system is usually perceived to be the less mature and most expensive part. Comparing different hybrid systems is considerably more complicated and will not be treated in this report.

Using the additional concepts of monolithic and modular reactor scaling, we then have a relatively simple means of predicting how one can increase the capacities (exhaust-gas flow rate or amount of pollutants treated) of different types of NTP reactors and how one can estimate the energy use/cost associated with the scaled-up reactor.

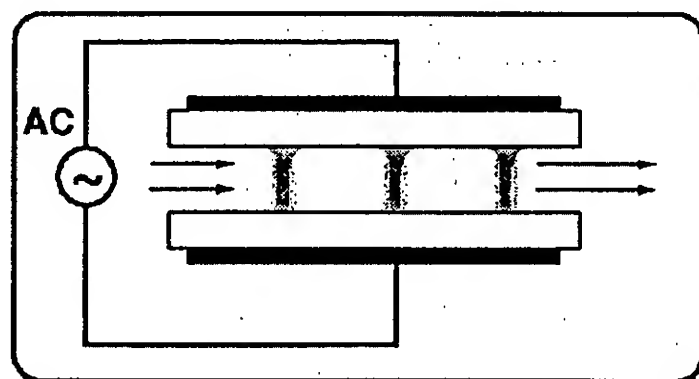
A figure of merit (the energy cost per pollutant molecule removed) has been introduced and we have shown how this figure of merit is related to some basic NTP reactor performance criteria - namely the plasma specific energy \bar{E} and the degree of pollutant removal, frequently expressed as $\ln([X]/[X]_0)$. The figure of merit is the same for either a monolithic or modular NTP reactor. However, the overall system cost scaling is likely to be very different for each of these types of scaling methodologies (and should be treated in a future report on system economics).

This report has served as an introduction to some basic scaling and optimization concepts - future reports (and the existing companion report from McMaster University) will further explore these concepts for particular reactors and reactor systems and architectures.

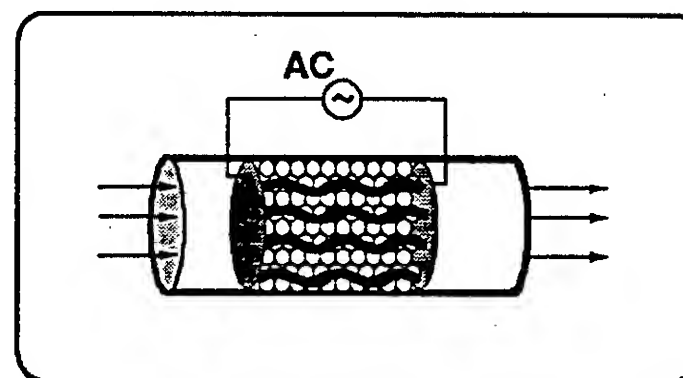
References

1. See articles in *Non-Thermal Plasma Techniques for Pollution Control, NATO ASI Series, Vol. G34, Parts A & B*, edited by B.M. Penetrante and S.E. Schultheis, Springer-Verlag, Berlin & Heidelberg (1993).
2. L.A. Rosocha, "Processing of Hazardous Chemicals Using Silent Electrical Discharge Plasmas," Chapter 11 in *Environmental Aspects in Plasma Science*, edited by W. Manheimer, L.E. Sugiyama, and T.H. Stix, American Institute of Physics Press, Woodbury, NY (1997).
3. G.E. Vogtlin, J.N. Bardsley, K.E. Freytag, B.M. Penetrante, and P.A. Vitello, "Non-Thermal Discharge Processing of Gaseous Pollutants," *Proceeding of First International EPRI/NSF Symposium on Advanced Oxidation*, EPRI TR-102927-V2 (1993).
4. D. Evans, L.A. Rosocha, G.K. Anderson, J.J. Coogan and M.J. Kushner, "Plasma remediation of trichloroethylene in silent discharge plasmas", *J. Appl. Phys.* **74** (9), pp. 5378-5386 (1993).
5. Z. Falkenstein, "Fundamental Studies on the Combined (V)UV-Non-Thermal-Plasma Treatment of Air Pollutants," Thesis, University of Karlsruhe & Los Alamos National Laboratory, LA-UR-96-2219 (July 1996).
6. B.M. Penetrante, M.C. Hsiao, J.N. Bardsley, B.T. Merritt, G.E. Vogtlin, P.H. Wallman, A. Kuthi, C.P. Burkhart, and J.R. Bayless, "Electron beam and pulsed corona processing of carbon tetrachloride in atmospheric pressure gas streams," *Physics Lett.* **A209**, pp. 69-77 (1995).
7. D.G. Storch, M.B. Chang, M.J. Rood, and M.J. Kushner, "Modeling and diagnostics of dielectric barrier discharge destruction of CCl_4 ," *Unpublished progress report to Los Alamos National Laboratory* (1991).
8. J.R. Bolton, K.G. Bircher, W. Tumas, and C.A. Tolman, "Figures-of-Merit for the Technical Development and Application of Advanced Oxidation Processes," *Journal of Advanced Oxidation Technologies*, **1**, pp. 13-17 (1996).

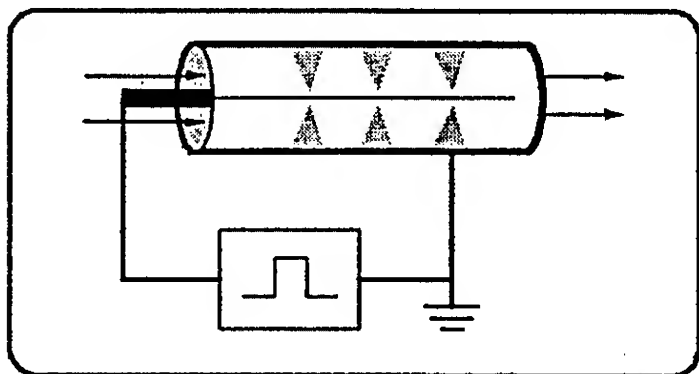
9. L.A. Rosocha, "Non-Thermal Plasmas as Gas-Phase Advanced Oxidation Processes," presented at Second International Symposium on Non-Thermal Plasma Technology for Pollution Control, Salvador, Brazil (August 11-15, 1997).
10. L.A. Rosocha, J.J. Coogan, R.A. Korzekwa, D.A. Secker, R.F. Riemers, P.G. Herrmann, P.J. Chase, M.P. Gross, and M.R. Jones, "Field Demonstration and Commercialization of Silent Discharge Plasma Air Pollutant Control Technology", *Proceedings of 2nd International EPRI/NSF Symposium on Environmental Applications of Advanced Oxidation Technologies*, pp. (Section 5) 107-121, Electric Power Research Institute (September 1997).
11. J.J. Coogan, A.S. Jassal, "Silent Discharge Plasma (SDP) for Point-of-Use (POU) Abatement of Volatile Organic Compound (VOC) Emissions: Final Report (ESHC003)", SEMATECH Report 97023244A-ENG (February 1997).
12. B.M. Penetrante, "Fundamental Limits on Chemical Reduction of NO_x by Non-Thermal Plasmas," presented at Second International Symposium on Non-Thermal Plasma Technology for Pollution Control, Salvador, Brazil (August 11-15, 1997).
13. O. Wolf et al, "Experimental Investigations of the Removal of Toxic Exhaust Gas Components by Dielectric Barrier Discharges," *Proceedings of 7th Bundesdeutsche Fachtagung für Plasmatechnologie (BFPT-7)*, Poster P 85, (1996).



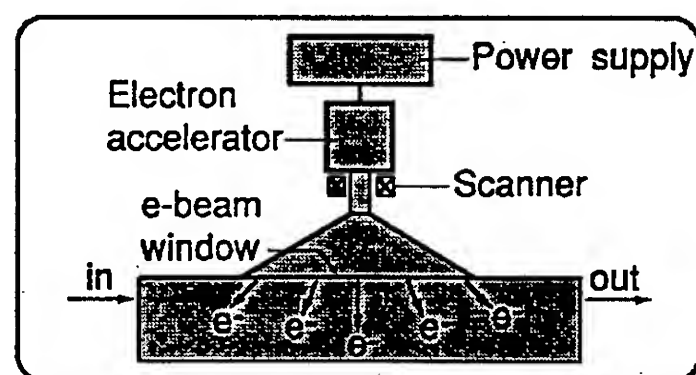
**Silent discharge
(dielectric-barrier discharge)**



**Electrified
packed bed**



Pulsed or DC corona



Electron beam

Figure 1: Commonly-employed NTP reactors.

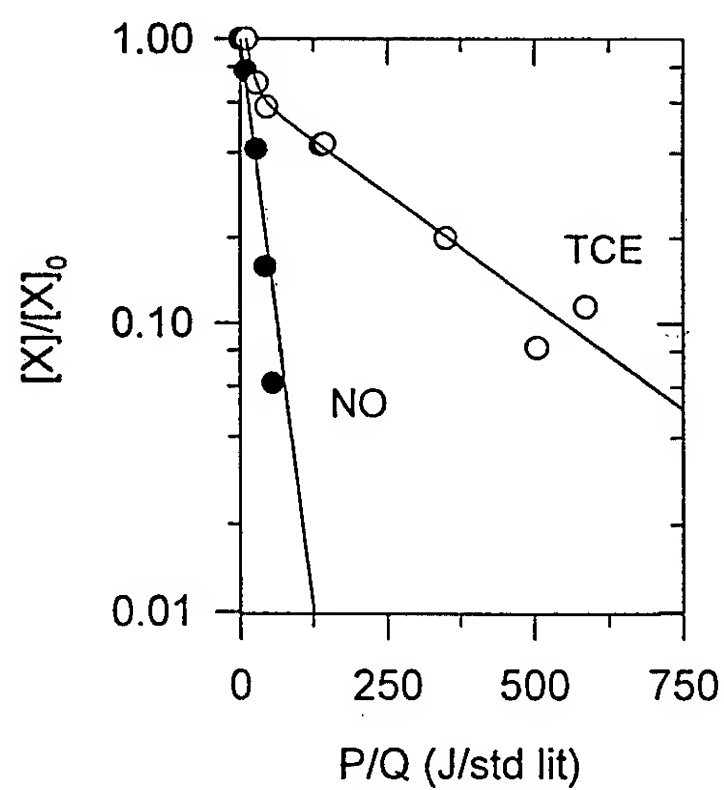


Figure 2: Decomposition plots for 400 ppm NO in simulated engine-exhaust gas after Wolf et al [13] and 190 ppm TCE in humid air after Falkenstein [5].

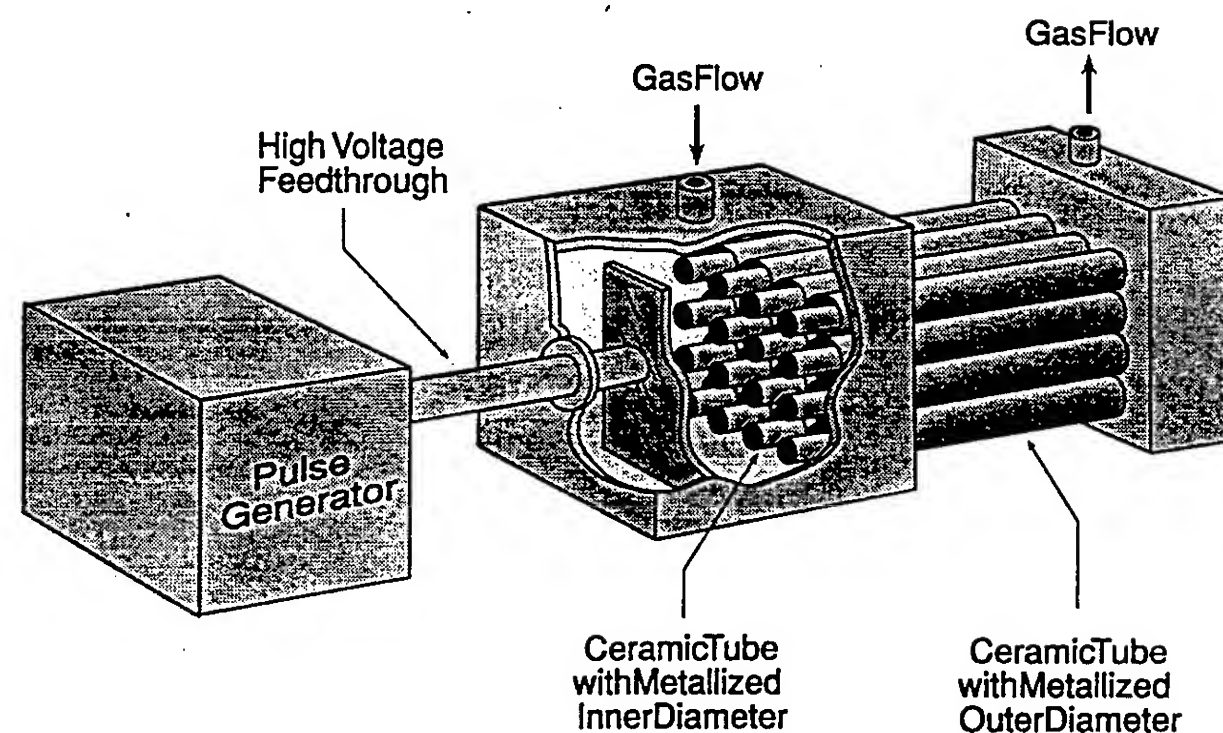


Figure 3: Modular NTP-reactor scaling using cylindrical barrier-discharge reactors.

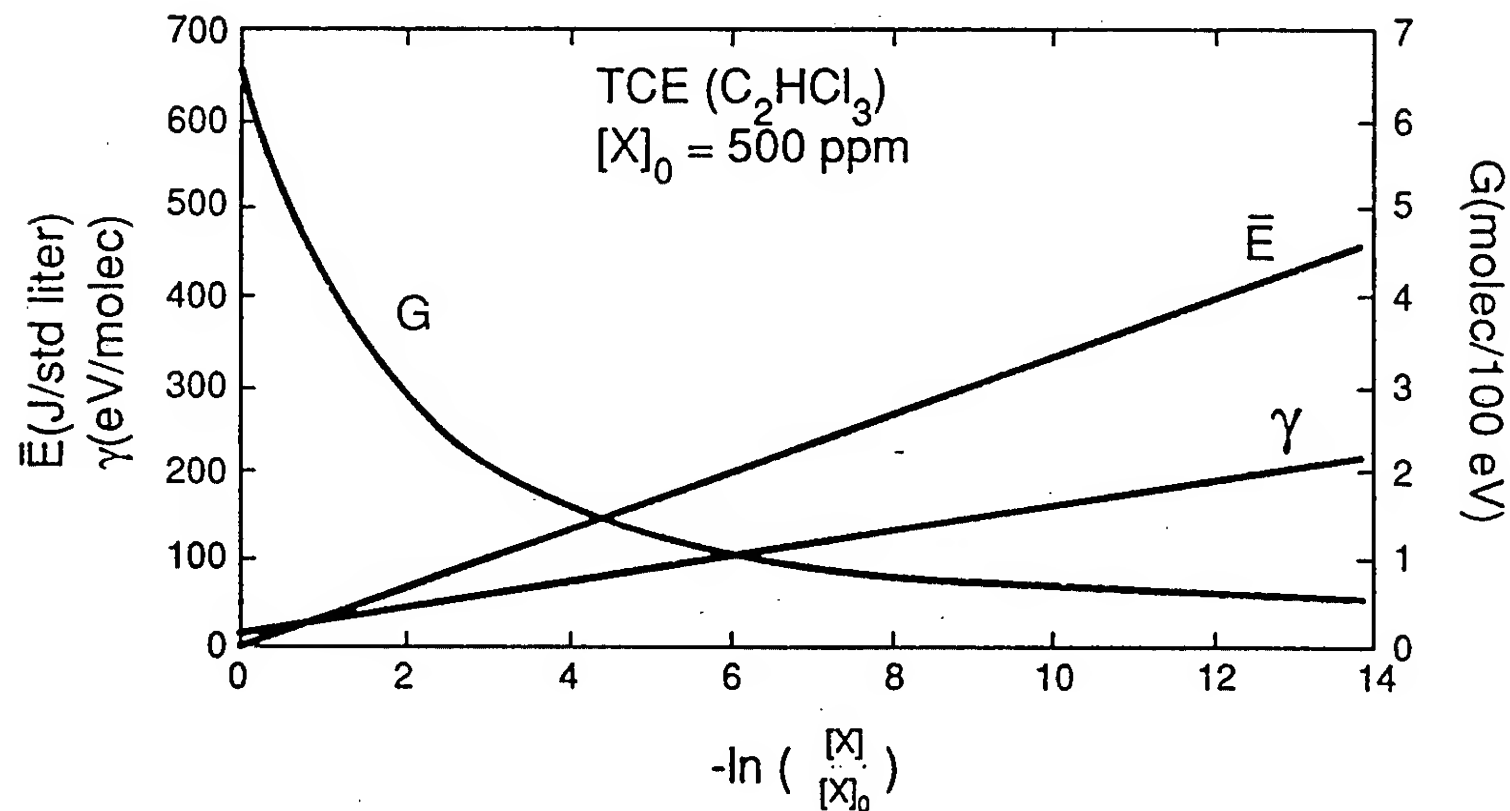


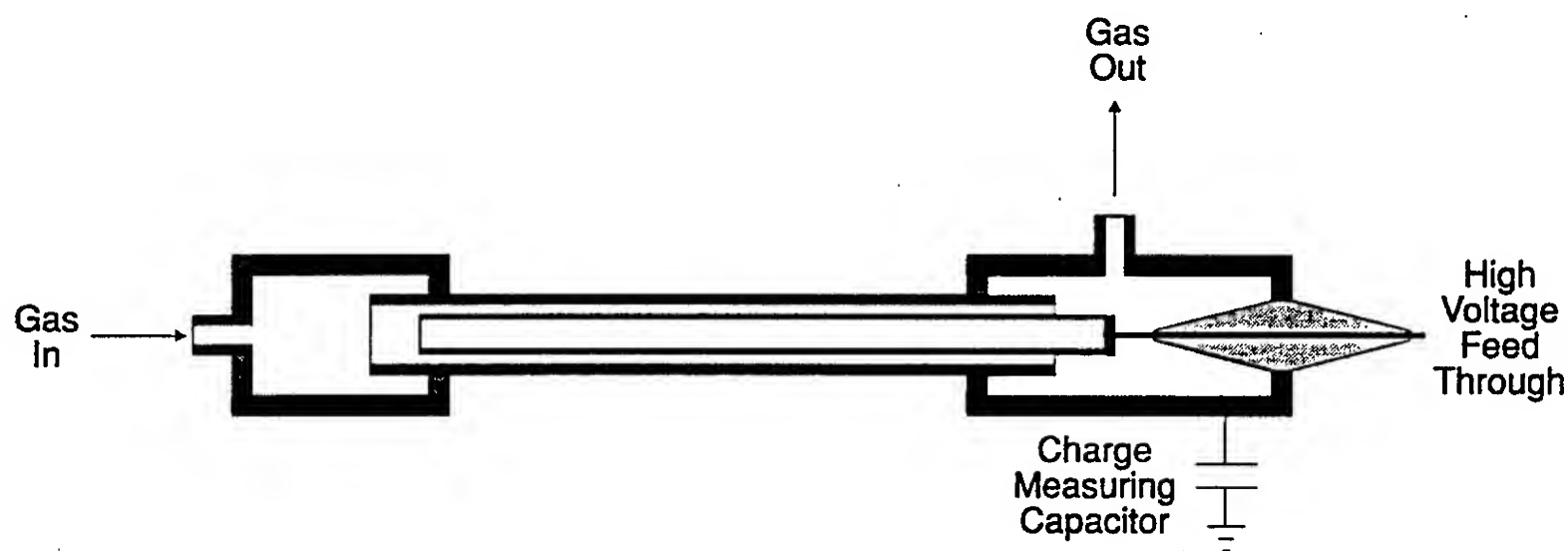
Figure 4: Plasma energy density and figure-of-merit plots for the representative chlorinated solvent TCE, under the model conditions of 80:20 Ar-O₂ gas mixture and $\beta = 33$ J/lit. A β -value of approximately 50 J/lit is typical of nitric oxide (NO) in air, using electrical discharges. As the degree of removal increases, the energy density and energy cost per molecule removed increase.

Appendix

High-Temperature, Ceramic Double-Dielectric-Barrier Non-Thermal Plasma Cell Summary Test Results

In using the modular scaling approach, several identical reactor modules are combined in parallel to achieve a higher capacity. Actual engine exhaust emissions streams containing NO_x are likely to be characterized by relatively high gas temperatures (e.g., perhaps in the range 300 - 500 C). To provide a prototype for a modular system, we have constructed and initially tested a cylindrical, ceramic-dielectric, silent electrical discharge NTP cell. This design is intended to provide a more robust plasma cell, capable of operating at the elevated temperatures likely to be encountered in actual field tests on diesel motor-generator or JETC exhausts.

The figure below illustrates the modular prototype cell. It is constructed of ceramic tubes (alumina), which are metalized to provide the necessary electrodes. This particular cell is approximately 5 cm in diameter and 76 cm in length (without the gas manifolds and feedthroughs). The specific energy deposited in the plasma is determined using a combination of high voltage probe and charge-measuring capacitor.



The cell was characterized at different temperatures and power levels, using different feed gases. The summary results are presented below. It should be emphasized that these are preliminary results - no attempt has been made to optimize the performance of the prototype.

At the highest operating temperature attempted (300 C), a power level of 100 W was easily achieved in dry air. Combining this figure with the 5 lit/min gas flow rate gives a plasma specific energy of 1200 J/lit. Such a specific energy is quite sufficient for removing many VOCs and is a factor of 24 greater than the one e-fold specific energy typically measured for NO removal in electrical-discharge driven NTP reactors (β -value of 50 J/lit). If we assume a requirement for one e-fold removal (63% of NO removed), then the 5 lit/min flow rate can be easily increased to 120 lit/min for this unoptimized prototype module.

- The cell was initially run in open air with 5 lit/min N_2 at 200W (4 kHz). Within 10 min, the temperature on the outside surface of the cell rose to 82 C until the power supply shut down. It

appears that with only a thin layer of nickel for an electrode, the heat transfer from the discharge is lower than with thick electrodes (perhaps due to the thermal mass). After that, the discharge was very unstable at 4 kHz, so the electrical drive circuit was adjusted and the cell was run at 1 kHz and 100 W.

- At approximately 100 C data was taken for nitrogen, dry air, and argon at 5 lit/min. The power was 100 W for nitrogen and dry air and 20 W for argon. The power level at which the power supply shut down (most probably due to an arc between the internal high voltage feed and the gas manifold) was 200 W for nitrogen and air and 30 W for argon.
- The temperature was raised to approximately 200 C using the oven and again data was taken for nitrogen, dry air, and argon at 5 lit/min. The power was 100 W for nitrogen and dry air and 15 W for argon. The power level at which the power supply shut down (most probably due to an arc between the internal high voltage feed and the gas manifold) was 180 W for nitrogen and air and 20 W for argon.
- The temperature was raised further to approximately 300 C using the oven and again data was taken for nitrogen, dry air, and argon at 5 lit/min. The power was 100 W for nitrogen and dry air and 15 W for argon. The power level at which the power supply shut down (most probably due to an arc between the internal high voltage feed and the gas manifold) was 140 W for nitrogen, 160 W for air, and 18 W for argon.